

SECTION 3.0

BACKGROUND INFORMATION

3.1 NATURE OF POLLUTANT

Benzene is a clear, colorless, aromatic hydrocarbon that has a characteristic sickly sweet odor. It is both volatile and flammable. Chemical identification information for benzene is found in Table-3-1. Selected physical and chemical properties of benzene are presented in Table 3-2 .⁴⁻⁷

Benzene contains 92.3 percent carbon and 7.7 percent hydrogen (by mass). The benzene molecule is represented by a hexagon formed by six sets of carbon and hydrogen atoms bonded together with alternating single and double bonds.

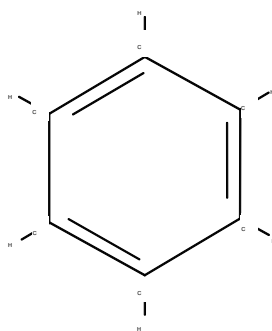


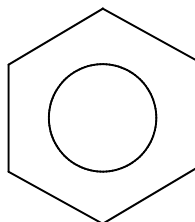
TABLE 3-1. CHEMICAL IDENTIFICATION OF BENZENE

Chemical Name	Benzene
Synonyms	Benzol, phenyl hydride, coal naphtha, phene, benxole, cyclohexatriene
Molecular formula	C ₆ H ₆
Identification numbers ^a	
CAS Registry	71-43-2
NIOSH RTECS	CY 1400000
DOT/UN/NA	UN 1114; Benzene (Benzol)
DOT Designation	Flammable liquid

Source: References 4 and 5.

^a Chemical Abstract Services (CAS); National Institute of Occupational Safety and Health (NIOSH); Registry of Toxic Effects of Chemical Substances (RTECS); Department of Transportation/United Nations/North American (DOT/UN/NA).

The chemical behavior of benzene indicates that the benzene molecule is more realistically represented as a resonance-stabilized structure:



in which the carbon-to-carbon bonds are identical. The benzene molecule is the cornerstone for aromatic compounds, all of which contain one or more benzene rings.⁸

Because of its resonance properties, benzene is highly stable for an unsaturated hydrocarbon. However, it does react with other compounds, primarily by substitution and, to a lesser degree, by addition. Some reactions can rupture the molecule or result in other groups cleaving to the molecule. Through all these types of reactions, many commercial chemicals are produced from benzene.⁸ The most common commercial grade of benzene contains 50 to

TABLE 3-2. PHYSICAL AND CHEMICAL PROPERTIES OF BENZENE

Property	Value
Molecular weight	0.17 lbs (78.12 g)
Melting point	41.9°F (5.5°C)
Boiling point at 1 atmosphere (760 mm Hg)	176.18°F (80.1°C)
Density, at 68°F (20°C)	0.0141 lb/ft ³ (0.8794 g/cm ³)
Physical state (ambient conditions)	Liquid
Color	Clear
Odor	Characteristic
Viscosity (absolute) at 68°F (20°C)	0.6468 cP
Surface tension at 77°F (25°C)	0.033 g/cm ³ (28.18 dynes/cm ³)
Heat of vaporization at 176.18°F (80.100°C)	33.871 KJ/Kg·mol (8095 Kcal/Kg·mol)
Heat of combustion at constant pressure and 77°F (25°C) (liquid C ₆ H ₆ to liquid H ₂ O and gaseous CO ₂)	41.836 KJ/g (9.999 Kcal/g)
Odor threshold	0.875 ppm
Solubility:	
Water at 77°F (25°C)	Very slightly soluble (0.180 g/100 mL, 1800 ppm)
Organic Solvents	Soluble in alcohol, ether, acetone, carbon tetrachloride, carbon disulfide, and acetic acid
Vapor pressure at 77°F (25°C)	95.2 mm Hg (12.7 kPa)
Auto ignition temperature	1044°F (562°C)
Flashpoint	12°F (-11.1°C) (closed cup)
Conversion factors (Vapor weight to volume)	1 ppm = 319 mg/m ³ at 77°F (25°C); 1 mg/L = 313 ppm

Source: References 4, 5, 6, and 7.

100 percent benzene, the remainder consisting of toluene, xylene, and other constituents that distill below 248°F (120°C).⁴

Laboratory evaluations indicate that benzene is minimally photochemically reactive in the atmosphere compared to the reactivity of other hydrocarbons. Reactivity can be determined by comparing the influence that different hydrocarbons have on the oxidation rate of nitric oxide (NO) to nitrogen dioxide (NO₂), or the relative degradation rate of various hydrocarbons when reacted with hydroxyl radicals (OH), atomic oxygen or ozone. For example, based on the NO oxidation test, the photochemical reactivity rate of benzene was determined to be one-tenth that of propylene and one-third that of n-hexane.⁹

Benzene shows long-term stability in the atmosphere.⁸ Oxidation of benzene will occur only under extreme conditions involving a catalyst or elevated temperature or pressure. Photolysis is possible only in the presence of sensitizers and is dependent on wavelength absorption. Benzene does not absorb wavelengths longer than 1.1×10^{-5} inches (in) (275 nanometers [nm]).⁸

In laboratory evaluation, benzene is predicted to form phenols and ring cleavage products when reacted with OH, and to form quinone and ring cleavage products when reacted with aromatic hydrogen.⁶ Other products that are predicted to form from indirect reactions with benzene in the atmosphere include aldehydes, peroxides, and epoxides. Photodegradation of NO₂ produces atomic oxygen, which can react with atmospheric benzene to form phenols.⁹

3.2 OVERVIEW OF PRODUCTION AND USE

During the eighteenth century, benzene was discovered to be a component of oil, gas, coal tar, and coal gas. The commercial production of benzene from coal carbonization began in the United States around 1941. It was used primarily as feedstock in the chemical manufacturing industry.¹⁰ For United States industries, benzene is currently produced in the United States, the Virgin Islands, and Puerto Rico by 26 companies at

36 manufacturing facilities.¹¹ The majority of benzene production facilities in the United States are found in the vicinity of crude oil sources, predominantly located around the Texas and Louisiana Gulf coast. They are also scattered throughout Kentucky, Pennsylvania, Ohio, Illinois, and New Jersey.¹¹

Domestic benzene production in 1992 was estimated at 2,350 million gallons (gal) (8,896 million L).¹¹ Production was expected to increase by approximately 3 to 3.5 percent per year through 1994. Exports of benzene in 1993 were about 23 million gal (87 million L), around 1 percent of the total amount produced in the United States.¹²

Benzene is produced domestically by five major processes.¹² Approximately 45 percent of the benzene consumed in the United States is produced by the catalytic reforming/separation process.¹¹ With this process, the naphtha portion of crude oil is mixed with hydrogen, heated, and sent through catalytic reactors.¹³ The effluent enters a separator while the hydrogen is flashed off.¹³ The resulting liquid is fractionated and the light ends (C₁ to C₄) are split. Catalytic reformat, from which aromatics are extracted, is the product.¹³

Approximately 22 percent of the benzene produced in the United States is derived from ethylene production.¹¹ Pyrolysis gasoline is a by-product formed from the steam cracking of natural gas concentrates, heavy naphthas, or gas oils to produce ethylene.¹⁴

Toluene dealkylation or toluene disproportionation processes account for another 25 percent of the United States production of benzene.¹¹ Toluene dealkylation produces benzene and methane from toluene or toluene-rich hydrocarbons through cracking processes using heat and hydrogen. The process may be either fixed-bed catalyst or thermal. Toluene disproportionation produces benzene and xylenes as co-products from toluene using similar processes.¹⁵

Three percent of benzene produced in the United States is derived from coke oven light oil distillation at coke by-product plants.¹¹ Light oil is recovered from coke oven

gas, usually by continuous countercurrent absorption in a high-boiling liquid from which it is stripped by steam distillation.⁹ A light oil scrubber or spray tower removes the light oil from coke oven gas.¹⁰ Benzene is recovered from the light oil by a number of processes, including fractionating to remove the lighter and heavier hydrocarbons, hydrogenation, and conventional distillation.

Finally, about 2 percent of benzene produced in the United States is derived as a coproduct from xylene isomerization.¹¹ Figure 3-1 presents a simplified production and use tree for benzene. Each major production process is shown, along with the percent of benzene derived from each process. The primary uses of benzene and the percentage for each use are also given in the figure.

The major use of benzene is still as a feedstock for chemical production, as in the manufacture of ethylbenzene (and styrene). In 1992, the manufacture of ethylbenzene (and styrene) accounted for 53 percent of benzene consumption.¹² Ethylbenzene is formed by reacting benzene with ethylene and propylene using a catalyst such as anhydrous aluminum chloride or solid phosphoric acid.⁸ Styrene is the product of dehydrogenation of ethylbenzene.⁹

Twenty-three percent of the benzene supply is used to produce cumene.¹² Cumene is produced from benzene alkylation with propylene using solid phosphoric acid as a catalyst.⁷ Cumene is oxidized to produce phenols and acetone.¹² Phenol is used to make resins and resin intermediates for epoxies and polycarbonates, and caprolactam for nylon.¹² Acetone is used to make solvents and plastics.¹⁶

Cyclohexane production accounts for 13 percent of benzene use.¹² Cyclohexane is produced by reducing benzene hydrogenated vapors using a nickel catalyst at 392 °F (200 °C). Almost all of cyclohexane is used to make nylon or nylon intermediates.¹⁷

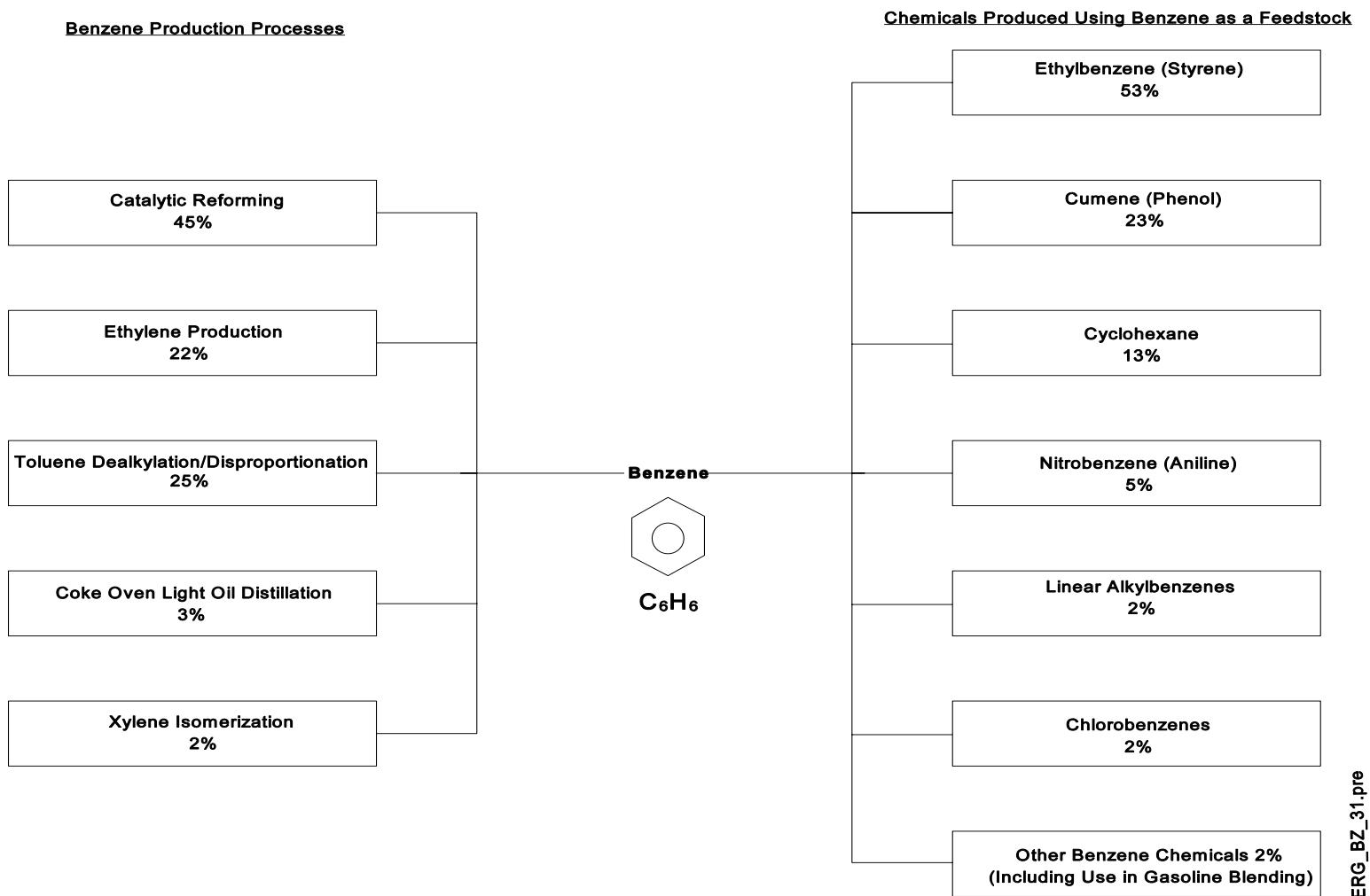


Figure 3-1. Production and Use Tree for Benzene

Source: References 11 and 12.

The production of nitrobenzene, from which aniline is made, accounts for 5 percent of benzene consumption. Nitrobenzene is produced by the nitration of benzene with a concentrated acid mixture of nitric and sulfuric acid. Nitrobenzene is reduced to form aniline.¹⁰ Aniline, in turn, is used to manufacture isocyanates for polyurethane foams, plastics, and dyes.¹⁸

Chlorobenzene production accounts for 2 percent of benzene use. The halogenation of hot benzene with chlorine yields chlorobenzene. Monochlorobenzene and dichlorobenzene are produced by halogenation with chlorine using a molybdenum chloride catalyst.¹⁹

The remainder of the benzene produced is consumed in the production of other chemicals. Other benzene-derived chemicals include linear alkylbenzene, resorcinol, and hydroquinone.

Though much of the benzene consumed in the United States is used to manufacture chemicals, another important use is in gasoline blending. Aromatic hydrocarbons, including benzene, are added to vehicle fuels to enhance octane value. As lead content of fuels is reduced, the amount of aromatic hydrocarbons is increased to maintain octane rating, such that the benzene content in gasoline was increased in recent years.⁴ The concentration of benzene in refined gasoline depends on many variables, such as gasoline grade, refinery location and processes, and crude source.⁶ The various sources of benzene emissions associated with gasoline marketing are discussed in Section 6.0, and benzene emissions associated with motor vehicles are discussed in Section 8.0 of this document.

3.3 OVERVIEW OF EMISSIONS

Sources of benzene emissions from its production and uses are typical of those found at any chemical production facility:

- Process vents;

- Equipment leaks;
- Waste streams (secondary sources);
- Transfer and storage; and
- Accidental or emergency releases.

These sources of benzene emissions are described in Sections 4.0 and 5.0 of this document.

Miscellaneous sources of benzene including oil and gas production, glycol dehydrators, petroleum refineries, gasoline marketing, POTWs, landfills, and miscellaneous manufacturing processes are addressed in Section 6.0. Combustion sources emitting benzene are addressed in Section 7.0. Section 8.0 presents a discussion of benzene emissions from mobile sources. Recent work by the EPA Office of Mobile Sources on benzene in vehicle exhaust resulted in revised emission factors.²⁰ For off-road vehicles, EPA has also completed a recent study to estimate emissions.